

UDC 666.768-12

## CORUNDUM FILTERING CERAMIC WITH PHOSPHATE BINDERS

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Translated from *Steklo i Keramika*, No. 8, pp. 28 – 31, August, 2008.

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The influence of different pore-forming additives in the form of regenerated Claus catalyst and coke on the physical – technical characteristics and permeability of the structure of corundum ceramic with phosphate binder is investigated. Samples with high permeability, close to monostructural samples with respect to the transport pore diameter distribution, are obtained on the basis of an analysis of gas-liquid porometry data.

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A great deal of attention is now being devoted to the development of ceramic filtering materials with regulatable pore structure.

It is well-known that materials with high mechanical strength and low CLTE, making it possible for ceramic filters to retain their dimensions and withstand sharp heat cycling loads during operation, are effective in high temperature filtration processes.

The structures being developed on the basis of phosphate binders are distinguished by the fact that they retain their structural strength at high temperatures in air and high heat resistance, which in most cases is due to the low (or zero) CLTE. At the same time, the phosphates formed (pentavalent phosphorus compounds) are by nature some of the safest compounds known to man.

The technology for obtaining ceramics with phosphate binders has been well mastered. Compaction occurs as a result of chemical reactions between phosphoric acid and oxide compounds in the charge as well as due to physical processes occurring in solid- and liquid-phase sintering.

The effect of different binders on the thermomechanical characteristics of a material has now been investigated. As a result, a corundum ceramic with phosphate binders which possesses unique properties and does not shrink has been obtained. In addition, the calcination processes are more cost-effective than for ceramic binders. However, questions concerning the study of the porosity of such a material are limited by the creation of heat-insulating ceramic with closed porosity.

In developing materials intended for use as filtering elements, a criterion of their applicability, together with me-

chanical strength and heat resistance, is the presence of a transport pore structure with a narrow distribution, which ensures a prescribed selectivity and production capacity of purification processes.

The objective of the present work is to develop mass compositions and a technology for obtaining filtering corundum ceramic with phosphate binder and a narrow diameter distribution of permeable pores. A comparative study is performed of the effect of different framework- and pore-forming additives on the physical – technical characteristics of ceramic samples as well as on the formation of a permeable structure of a corundum ceramic with a phosphate binder. A widely used technological technique where a ceramic paste consisting of filler and a dispersed binder is formed was used to produce porous structures.

A filtering ceramic with phosphate binders is a composite material consisting of dispersed particles of the filler and matrix-binder. The filler consists of fractionated grains of oxide material whose properties remain unchanged during calcination. The other part consists of the matrix-binder with a complex chemical composition, whose phase state and physical – chemical properties change in the course of the technological operations involved in the creation of a pore structure.

Aluminum oxide powder melted in a solar furnace and separated into fractions 250 – 500, 125 – 250, 80 – 125, 63 – 80, and less than 50  $\mu\text{m}$  was used as the filler to form samples of ceramic filters. Radiative solar heating possesses the following characteristics — ease of reaching high temperatures and instantaneous control, which make it possible to obtain prescribed rates of heating and cooling of melts. Experience shows that materials melted in a solar furnace and quenched in water are much easier to grind.

The initial compositions for obtaining ceramic samples lie in the range of the following multi-component systems:  
fused corundum – kaolin clay – phosphoric acid;

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fused corundum – kaolin clay – phosphoric acid – alumina;

fused corundum – kaolin clay – phosphoric acid – alumina – gypsum;

fused corundum – kaolin clay – phosphoric acid – alumina – gypsum – coke.

Factors which are reflected in the literature were taken into account when developing compositions with permeable structure [1]: the amount of phosphate binder with respect to filler, ratio of inert grains of filler and clay binder, dispersity of the powdered additives introduced, and concentration of phosphoric acid.

The initial ceramic paste for fabricating filtering articles contains dispersed powder of fused aluminum oxide (at least 80%<sup>2</sup>) and a clay binder. Samples with monodispersed and polydispersed filler were investigated. When the paste was prepared, it was mixed with a 70% solution of phosphoric acid in the amount 10–11% (above 100%). Angrenskoe kaolin was used as the clay binder. The permeability of the structure was changed by introducing different pore- and framework-forming additives. Aluminum oxide in the amorphous state which had dispersity less than 1  $\mu\text{m}$  and high reactivity and was obtained from the spent catalyst of the Claus process by thermal removal of sulfur contaminants from it, served as the framework-forming additive. The pore-forming additives were gypsum (density of the forming phase is high compared with the initial phases) and coke (consumable phase).

The spent aluminum oxide catalysts from the Claus process, containing at least 95–99% aluminum oxide, introduced into the binder interacts with phosphoric acid, forming a bonding material, which in a composition with kaolin clay forms a nonshrinking strong framework with a polymineral composition, which strengthens the porous structure.

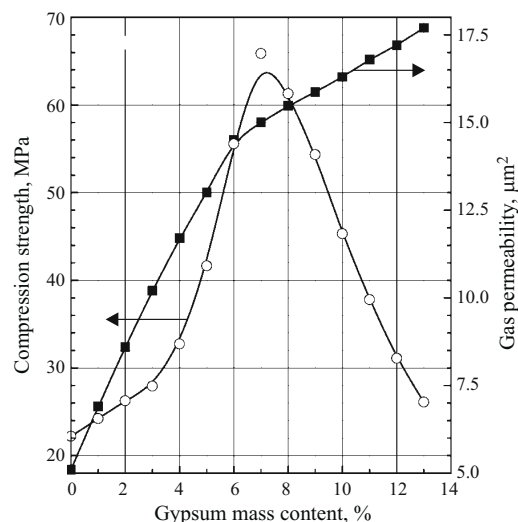
Apparently, the introduction of gypsum into the composition creates a porous structure by forming a series of compounds in the system  $\text{CaO} - \text{Al}_2\text{O}_3 - \text{SiO}_2 - \text{P}_2\text{O}_5$ , whose density is higher than that of calcite kaolin, as a result of which voids capable of additional porization of the phosphate-ceramic binder appear. All compounds of this system possess high heat resistance with melting onset and cessation temperatures 1788 and 2083 K [2].

Generally accepted methods were used to investigate the properties of the filters obtained. The open porosity, linear shrinkage, compression strength, maximum pore size, and air permeability were determined.

The gas-liquid porometry was used to evaluate the parameters of the pore structure of the material [3].

Gas-liquid porometry makes it possible to determine clearly and with a high degree of accuracy not only the maximum size of pores but also the entire range of diameters of filtering pores and their size distribution.

The crux of the method consists in combining the bubble technique (GOST R 50516–93) and the method used to de-



**Fig. 1.** Effect of gypsum content in the initial material on the properties of articles (calcination temperature 1200°C, content of fused corundum grains with dispersity 250–500  $\mu\text{m}$  — 80%, spent Claus catalyst content in the binder — 2% and phosphoric acid — 10%, above 100%).

termine the permeability of gases and liquids (GOST 25283–82). For this, two flow characteristics of “dry” and “wet” samples are measured and constructed in the same coordinates in a wide range of pressures of the entering gas. Then, calculations performed by the method of tangents are performed to determine the sizes and volumes of the filtering pores.

The temperature regime of calcination was chosen beforehand on the basis of operational data, which make it possible to evaluate the strength of the ceramic. Strength remains low for all samples heat-treated up to 1000°C; a sharp increase in strength is observed at temperatures 1150–1200°C.

Measuring out the amount of regenerated Klaus catalyst which is added made it possible to synthesize ceramic with improved mechanical properties. The optimal quantity of additive is 2–4%, since this amount does not decrease the permeability of the filtering articles.

To obtain a composite material with a stronger porization effect, it is best to introduce over 5–7% gypsum. Above this amount the mechanical properties degrade, causing articles to swell because of volume changes accompanying the formation of chemical compounds (Fig. 1).

Thus, the problem of obtaining a strong, nonshrinking, filtering ceramic based on narrow-fraction fused corundum powders with gypsum and spent Claus catalyst added as the pore- and framework-forming components has been solved.

However, solving the problem of increasing the mechanical strength, it should not be forgotten that the main objective in developing a filtering ceramic is articles with high permeability. Consequently, subsequent investigations on obtaining nonshrinking ceramic with phosphate binders were

<sup>2</sup> Here and below — the mass content.

TABLE 1.

Sample*	Mass content of binder components, %					Calcination temperature, °C	Open porosity, %	Compression strength, MPa	Shrinkage, %	Gas permeability, μm <sup>2</sup>	Maximum size of filtering pores, μm (bubble method)
	Angrenskoe kaolin	alumina	gypsum	coke (above 100%)	70% H <sub>3</sub> PO <sub>4</sub> (above 100%)						
Filler fraction 250 – 500 μm											
1	20	—	—	—	10	1250	28.00	17.0	0	4.71	81.4
2	16	4	—	—	10	1200	32.00	23.0	0	4.86	76.2
3	11	2	7	—	10	1200	30.00	66.2	0	14.65	99.0
4	11	2	7	20	10	1150	46.00	20.7	0.8	22.48	123.8
Filler fraction 125 – 250 μm											
5	20	—	—	—	10	1200	35.46	11.2	0	2.00	43.0
6	16	4	—	—	10	1200	38.27	19.6	0	2.77	48.3
7	11	2	7	—	10	1200	37.21	64.0	0	8.81	69.1
8	11	2	7	20	10	1150	45.84	52.5	1.4	20.30	87.4
Filler fraction 80 – 125 μm											
9	20	—	—	—	10	1200	38.50	11.3	0	1.15	31.9
10	18	2	—	—	10	1200	45.43	16.2	0	2.10	34.9
11	11	2	7	—	10	1200	42.00	82.1	0	3.52	39.6
12	11	2	7	20	10	1150	50.93	59.5	1.4	13.33	67.5
Filler fraction 63 – 80 μm											
13	20	—	—	—	11	1200	38.16	11.3	0	1.00	24.1
14	18	2	—	—	11	1200	45.46	11.9	0	1.16	25.4
15	11	2	7	—	11	1200	46.63	79.2	0	4.28	41.3
16	11	2	7	20	11	1150	46.58	45.1	1.7	10.74	49.5
Filler fraction less than 50 μm											
17	20	—	—	—	11	1200	40.08	66.3	0	0.03	2.8
18	13	—	7	—	11	1200	36.80	150.0	0	0.07	6.0
19	13	—	7	20	11	1150	51.14	72.5	1.4	3.65	28.3

\* The content of the filler  $\text{Al}_2\text{O}_3$  (fused) was 80% in all cases.

directed toward improving its pore structure, specifically, increasing the permeability and creating a porous structure with a narrower size distribution of the filtering pores.

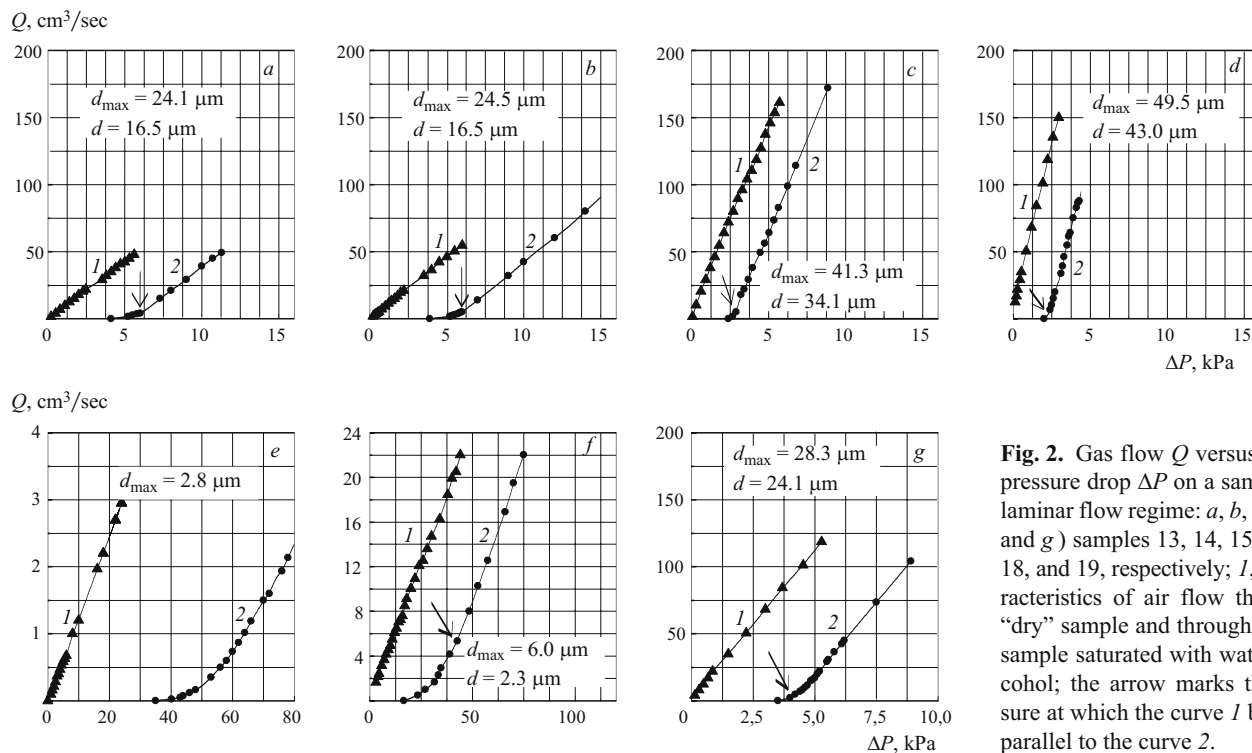
The effect of coke (a widely used pore-forming consumable additive) on the formation of a permeable structure of alumophosphate ceramic was investigated. A comparative analysis of the permeability of filtering samples without coke and with 20% coke added was performed. The initial compositions and properties of the filtering corundum ceramic and phosphate binder are presented in Table 1.

The maximum size  $d_{\text{max}}$  of permeable pores in samples of the filtering ceramic with no additives (samples 1, 5, 9, 13, 17) is determined by the grain size of fused corundum and is approximately one third of the grain size. When additives from any group are introduced, the diameter of the filtering pores increases. The largest increase is observed in samples with coke additives (4, 8, 12, 16).

Adding amorphous aluminum oxide in the form of spent Claus catalyst into the system has virtually no effect on the parameters of the pore structure which are studied, but on the

whole a positive growth dynamics of strength, porosity, and gas permeability of the samples (2, 6, 10, 14) is observed. Thus, there is no qualitative change in the chemical interaction of the components with phosphoric acid. Apparently, the reaction with kaolin is also determined by the interaction with aluminum oxide present in it. The introduction of aluminum oxide additives in amounts exceeding 4% degrades the mechanical properties at the prescribed calcination temperature. The  $\text{Al}_2\text{O}_3$  particles act as an inert filler material, since they do not form strong bonds with one another without phosphoric acid.

When gypsum is added, the properties change very strongly. An additive not only increases the strength of the ceramic by a factor of 5 – 6 but it also promotes the formation of a permeable pore structure, which is characterized by a sharp increase of permeability against a background of a lesser increase of the pore size  $d_{\text{max}}$  (samples 3, 7, 11, 15). Apparently, the chemical reactions in the system, which is characterized by triple and double low-melting eutectics, change the pore-space type. This occurs as a result of the for-



**Fig. 2.** Gas flow  $Q$  versus the gas pressure drop  $\Delta P$  on a sample in a laminar flow regime: a, b, c, d, e, f, and g) samples 13, 14, 15, 16, 17, 18, and 19, respectively; 1, 2) characteristics of air flow through a "dry" sample and through a "wet" sample saturated with water or alcohol; the arrow marks the pressure at which the curve 1 becomes parallel to the curve 2.

mation of new phases, whose density is higher than that of the initial phases.

The character of the dependence of the properties of the samples on the consumable additive in the form of coke is predictable: porosity increases to 45–50% and permeability increases by a factor of 2–5 with mechanical strength decreasing slightly.

Plots of the flow characteristics obtained by gas and liquid porometry reflect the size range of the filtering pores (Fig. 2). The pore-size distribution in a ceramic obtained without pore-forming additives and with the addition of Claus catalyst is similar. In Fig. 2a and b the flow characteristics of the "dry" and "wet" samples at the initial stage are not parallel, indicating a wide pore-size range. The sizes of the largest and smallest pores differ by approximately 50%. A filtering ceramic with finer purification cannot be obtained even with such a pore-size range (sample 17). In Fig. 2e, for this sample there is no section where the flow characteristics are parallel, attesting to a very wide and diffuse interval.

The plots reflecting the pore distribution for samples with gypsum and 20% coke as a consumable additive show a completely different picture. The size range of the filtering pores ( $d_{\max} - d$ ) has become narrower and does not exceed 25–30% (see Fig. 2c). The sample with added coke (see Fig. 2d) is similar to a monostructure with the same pore size ( $d_{\max}$  and  $d$  differ by 10–12%).

The data in Table 1 and Fig. 2 show the clear advantages of filtering properties of porous ceramic with phosphate binders with coke, as a consumable additive, and gypsum. The results show that the permeability of the ceramic depends on the interval of filtering pores ( $d_{\max} - d$ ). For exam-

ple, a structure with a narrower range of transport pores (see Fig. 2g) as compared with the structure shown in Fig. 2b results in an increase of the permeability from 1.16 to 3.65 with strength increasing at the same time by a factor of 6–7.

A successful technological solution for obtaining micro-filtering ceramic with pore size of several microns is introducing gypsum additives (see Fig. 2f). The introduction of coke into such structures gives an uncontrollable sharp increase of pore size by an order of magnitude, which, apparently, is due to the sizes of the coke particles themselves as well as the additional loosening of the structure as result of the volatilization of gaseous products from the combustion of coke (see Fig. 2g).

Thus, gas-liquid porometry data make it possible to evaluate and realize directed formation of porous structures of ceramic filters.

Paste compositions and the technology for introducing pore-forming additives based on gypsum and coke to obtain a filtering corundum ceramic based on a phosphate binder with a narrow distribution of the diameters of permeable pores have been developed.

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